COATINGS. ENAMELS

UDC 642.72:666.29.056

LEAD-FREE ENAMELS FOR DECORATION OF GLASS ARTICLES

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Translated from Steklo i Keramika, No. 9, pp. 25 – 27, September, 2004.

The optimum compositions of lead-free fluxes and enamels based on them are determined; their physiochemical properties are analyzed. The quantitative transformation of the enamel coating into solutions depending on the duration of the reactant effect is determined.

Decorating glass articles by ornamental enamels contributes to expanding the product range and improves the exterior appearance [1].

The majority of industrially used low-melting enamels for glass are lead-bearing, have a low spreading temperature, good luster, and a wide temperature interval of melting, which makes them most suitable for mass-scale decoration of glass products [2, 3].

However, the production and application of lead-bearing enamels in the industry is undesirable due to the toxic effect of lead compounds (the toxic materials of danger class 1, i.e., highly dangerous) on a human organism [4]. As a rule, the content of lead compounds on working places (in charging and melting of batches) exceeds the maximum permissible concentrations [5]. According to the current Sanitary Regulations SanPiN 13-3 RB 01, the maximum permissible quantity of lead in the working zone air should not exceed 0.02 mg/m^3, whereas the quantity released from decorative coatings registered in sanitary-chemical tests of glass products is equivalent to 0.03 mg/m^3.

The purpose of our study was to develop lead-free enamels for decorating glass articles made of sodium-potassium silicate glass. As an ornamental enamel consists of two parts, i.e., a vitreous base (flux) and a pigment, we first developed a lead-free low-melting flux of an optimum composition and then obtained tinted enamel based on this flux. The system selected for the flux based was (N_2O, K_2O) – BaO – CaO – ZnO – B_2O_3 – Al_2O_3 – P_2O_5 – TiO_2 – SiO_2 [6].

Batches were prepared using quartz sand, barium nitrate, boric acid, zinc white, sodium phosphate, potassium saltpeter, lithium carbonate, chalk, and titanium and aluminum oxides.

The glasses were melted in an electric furnace with silit heaters in corundise crucibles at 1000 – 1100°C with an exposure at the maximum temperature for 30 min. To obtain granulate, the solution was poured into water with subsequent drying. Glass powder was prepared by milling the granulate in a planetary mill for 6 h and separating the fraction of less than 40 μm.

The chemical composition of the developed fluxes varied within the following range (here and elsewhere, wt.%): 10.0 – 20.0 BaO, 10.0 – 17.0 SiO_2, 15.0 – 20.0 B_2O_3, 1.0 – 1.5 CaO, 20.0 – 40.0 ZnO, 1.0 – 6.0 TiO_2, 1.0 – 3.0 Li_2O, 1.0 – 3.5 K_2O, 3.0 – 5.0 Na_2O, 15.0 – 30.0 P_2O_5, 0 – 1.5 Al_2O_3.

We investigated several series of glasses, in which phosphor oxide was replaced by zinc oxide. The total content of zinc and phosphor oxides was 50%. Titanium and aluminum oxides were added to fluxes in an amount from 1.0 to 6.0 and from 1.0 to 1.5%, respectively. Lithium oxide in an amount from 1.0 to 3.0% was introduced from 1.0 to 3.0% instead of sodium and potassium oxides. The total content of alkali oxides ($Li_2O + Na_2O + K_2O$) was 11.5% and the concentration of the remaining oxides (BaO, B_2O_3, and CaO) was constant. The content of lithium oxide in fluxes 5, 6, 7, and 8 was 0.5, 2.0, 1.0, and 3.0%, respectively.

Fluxes 1 – 4 have low weight losses when treated with hot water and 2% sodium carbonate solution, and at the same time have high TCLE values, which causes crackle in glass coatings after their firing at 580°C.

The replacement of phosphor oxide by zinc oxide while increasing the content of titanium and aluminum oxides in fluxes decreases their TCLE and significantly improves the quality of the surface of heat-treated glass coating.

Estimating the effect of phosphor, zinc, titanium, aluminum, and lithium oxides in general on the properties of in-

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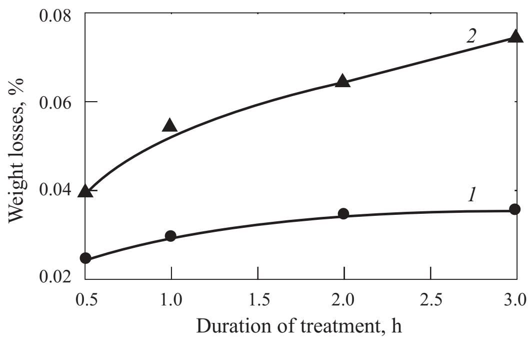

Fig. 1. Dependence of chemical resistance of flux 8 on treatment duration in hot (98°C) distilled water (*1*) and 2% solution of sodium carbonate (*2*).

vestigated flux and coatings based on them, it should be noted that the optimum parameters are seen in flux 8, which contains along with other oxides (%): 34.0 ZnO, 6.0 TiO_2, 1.5 Al_2O_3, and 3.0 Li_2O.

As a consequence of the research performed, composition 8, which has the optimum combination of physicochemical and technological properties, was selected as the vitreous base for enamels.

The TCLE of fluxes was measured using a DKV-4 quartz dilatometer on samples shaped as rods of diameter 4 and length 50 mm. The TCLE was calculated for the temperature interval of 20 – 400°C. The error of measuring the TCLE was ± 1.6% with reliability 0.95.

The softening start temperature and the flux density were measured using the standard methods [7], the chemical resistance of fluxes was determined by the granular method with respect to hot (98°C) distilled water and 2 % solution of sodium carbonate (GOST 10134.0-82-10134.3-872). The mean relative error of determination was ± 20%. The properties of the developed fluxes are listed in Table 1.

It can be seen from Fig. 1. that the dissolution of flux in hot water is slowed down and depends on the duration of treatment. Apparently, a protective layer is formed in the course of glass destruction, which consists of the destruction products. The silicates of metals (zinc, barium, etc.) coming into a contact with water become hydrolyzed and the insoluble products of hydrolysis are deposited on the sites of their formation. The surface layer has a protective effect and when its formation is completed, the process of glass destruction is self-inhibited [6]. The longer the effect of 2% sodium carbonate, the more substantial it is the weight loss of the flux.

Flux 8 was chosen as the optimum one regarding its physicochemical parameters: its TCLE is close to the TCLE of household glass, i.e., $85.5 \times 10^{-7}\ K^{-1}$ and its softening temperature is 478°C. A glass coating based on this flux after firing for 20 min at 580°C acquires a glossy surface and luster, does not have cracks or flaking, which makes it suitable as the base for enamels to be used on glass.

By means of selecting ratios between flux 8 and pigments, tinted enamels were developed and the effect of pigments on their physicochemical properties was investigated. The experiments used industrial ceramic pigments produced by the Dulevo paint factory. Increasing or decreasing a pigment content intensifies or weakens the color of the enamel coating. Too large pigment additives lead to oversaturation of the vitreous base mixtures, which prevents good fusion of glass coatings. The optimum content of the pigment in enamels of various colors amounted to 5 – 20% of the flux mass, whereupon the TCLE of the flux changed by no more than 2%. These studies indicated that mixing enamels of different colors produces additional half-tone compositions.

Enamels preliminary mixed with an organic binder containing oxyterpene resin, turpentine, and colophony were applied to household glass in hand painting and fired until the formation of a glossy coating. The optimum firing temperature for enamel coatings in a muffle furnace is 580 – 590°C with a 20 min exposure.

The chemical resistance of enamel coatings deposited on a glass substrate was determined based on their resistance to hot (98°C) water and 2% soda solution. The quantity of the reactant was equal to 5 cm^3 per cm^2 of the surface area of the sample. The weight loss of the sample converted to 100 cm^2 of surface area coated with enamel was determined from the formula:

$$a = \frac{A - B}{S} \times 100,$$

where A and B is the weight of the glass sample coated by enamel before and after the effect of the reactant, respectively, mg; S is the surface area of the sample coated with enamel, cm^2.

The weight losses of samples with a non-decorated surface can be neglected, since they are insignificant and lie within the measurement error limits.

TABLE 1

Flux	TCLE, $10^{-7}\ K^{-1}$	Softening temperature, °C	Chemical resistance: in hot (98°C) distilled water*	Chemical resistance: in 2% solution of Na_2CO_3*	Density, kg/m^3	Characteristics of glass coating**
1	90.2	471	0.069	0.089	3050	Cracks in coating
2	91.3	471	0.025	0.029	3250	The same
3	99.9	450	0.044	0.160	3080	″
4	95.0	466	0.047	0.040	3850	″
5	85.6	481	0.160	0.130	3090	High-quality coating
6	85.3	476	0.037	0.060	2460	The same
7	87.2	476	0.045	0.072	3140	″
8	85.5	478	0.030	0.055	2400	″

* For 1 h.

** After firing at 580°C with 20 min exposure.

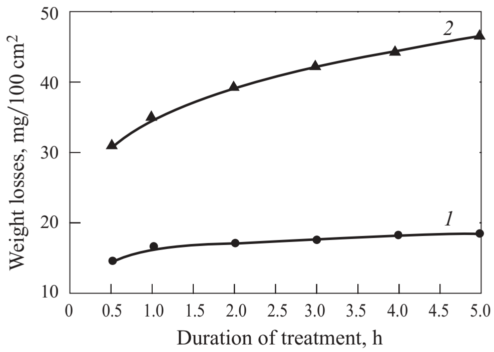

Fig. 2. Weight loss of samples of enamel coating containing 10% green pigment of the flux weight converted to 100 cm^2 surface area covered by enamel depending on the duration of treatment with hot (98°C) distilled water (*1*) and 2% solution of sodium carbonate (*2*).

It can be seen in Fig. 2 that the coating has low weight losses. Thus, the weight loss after 1 h of hot water treatment is 16.5 mg/100 cm^2, and after 2% sodium carbonate solution — 35 mg/100 cm^2. An increase in the pigment content in the coating to 20% modifies its chemical resistance by not more than 2 – 3%. According to TU RB 100029049.030 standard, the following requirements are imposed on enamels for decoration of the exterior surface of glass articles: admissible weight loss of the sample per 100 cm^2 surface area of enamel coating after 1 h treatment of 2% sodium carbonate solution not more than 100 – 200 mg, after treatment with hot (98°C) distilled water — 50 – 100 mg.

The visual evaluation of the surface of enamel coatings after 20 days of exposure in distilled water at room temperature demonstrated high water resistance of the enamels tested.

The enamels have been industrially tested on household glassware produced by the F. E. Dzerzhinskii Borisov Crystal Glass Works and are recommended for industrial production.

Thus, the new lead-free fluxes can be used as the base for ornamental enamels to be applied to glass.

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